



## Two stage pyrolysis-catalytic gasification of waste tyres: Influence of process parameters

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### ABSTRACT

The pyrolysis-catalytic steam gasification of waste tyres has been investigated using a two-stage fixed bed reactor. The catalyst used was  $\text{Ni}/\text{Al}_2\text{O}_3$ . The influence of the process parameters, catalyst:waste tyre ratio, gasification temperature and water injection rate on hydrogen production were investigated. The results indicated that the potential  $\text{H}_2$  production (conversion of the hydrogen in the tyre to hydrogen gas) was 7.19 wt.% when the catalyst:waste tyres ratio was 0.5 (g/g), which increased to 20.0 wt.% at the catalyst:waste tyres ratio of 2.0 (g/g). Increasing the gasification temperature from 600 to 900 °C was shown to increase gas yield from 14.3 wt.% to 56.8 wt.% and the potential  $\text{H}_2$  production increased from 3.2 to 13.1 wt.%. The steam flow rate, in terms of the amount of water injected, had a small but significant influence on the potential  $\text{H}_2$  production. The characteristics of the carbon deposited on the reacted catalysts were examined by temperature-programmed oxidation (TPO) and scanning electron microscopy (SEM) and were shown to consist of be monoatomic carbon and filamentous carbon. The amount of carbon deposited on the catalyst was reduced with an increase in the amount of catalyst used and the water content. However, the highest amount of coke deposited on the catalyst was 20.8 wt.% for the gasification temperature of 700 °C.

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### 1. Introduction

Waste tyre disposal continues to be an economic and environmental problem. It is estimated that 3.4 million tonnes per year of waste tyres are generated in Europe [1], 4.6 million tonnes in the U.S. [2], greater than 1 million tonnes in Japan [3] and around 5 million tonnes in China [4]. Such large tonnages of waste tyres represent a major potential energy resource. There have been several studies investigating the thermal processing of waste tyres for energy recovery, including combustion [5,6], gasification [7,8] and pyrolysis [9–11].

Gasification of waste tyres has been shown to generate high concentrations of hydrogen and methane in the product gases [8,12–15]. Hydrogen is of particular interest since it is projected to play a major role in future energy systems, since it is regarded as a clean energy source. Mastral et al. [13] proposed the pyrolysis of waste tyres to produce pyrolysis oil which was subsequently gasified using oxygen to produce high yield hydrogen. Such two-stage processes offer a promising route to hydrogen production since each stage can be optimally controlled and the second stage gasification process enables the introduction of steam and/or catalysts.

For example, using steam reforming of the produced gases from pyrolysis of waste tyres, a high yield of hydrogen can be obtained and by introducing catalysts, the hydrogen forming reaction rate can be optimised [16,17].

In our previous work, we have shown that nickel based catalysts with addition of other metals can produce high concentrations of hydrogen in the product gas [16,17]. In this paper, we extend that work to include the influence of process parameters on the production of hydrogen and other gases using a  $\text{Ni}/\text{Al}_2\text{O}_3$  catalyst for the pyrolysis-steam catalytic gasification of waste tyres. The process parameters investigated include catalyst:waste tyre ratio, gasification temperature and water injection rate and their influence on hydrogen production.

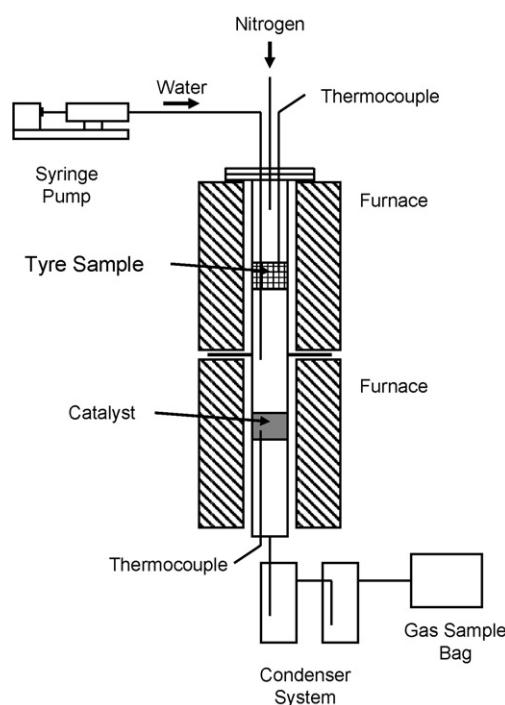
### 2. Experimental

#### 2.1. Materials

The waste tyres used in this study were from passenger cars and consisted of the rubber tread with steel removed and was shredded to a particle size of about 6 mm. The elemental analysis of the rubber of the tyres showed that the carbon, hydrogen, nitrogen, and sulphur contents were 86.4, 8.0, 0.5, 1.7 wt.%, respectively. The  $\text{Ni}/\text{Al}_2\text{O}_3$  catalyst was prepared by an incipient wetness method using  $\text{Al}_2\text{O}_3$  and an aqueous solution of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . All

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**Fig. 1.** Schematic diagram of the two stage pyrolysis-catalytic gasification experimental system.

materials, which were used in the catalyst preparation, were obtained from Sigma–Aldrich, U.K. After loading the nickel onto the  $\text{Al}_2\text{O}_3$  (10 wt.% Ni), the catalyst was dried at 105 °C overnight, and calcined at 500 °C for 3 h under an air atmosphere. The catalyst was sieved to granules with a size less than 0.212 mm.

## 2.2. Experimental system

Waste tyre pyrolysis-catalytic gasification was conducted using a two stage fixed bed reactor. The waste tyre was pyrolysed at 500 °C in the first stage and the evolved products were then passed directly to the second catalyst stage where the catalyst was located and where steam was introduced. Fig. 1 shows a schematic diagram of the reactor system. Approximately 1 g of waste tyre was loaded into the first stage reactor with different amounts of catalyst in the second stage gasification reactor depending on tyre:catalyst ratio. The catalyst:waste tyre ratios investigated were 0.5, 1.0, 1.5 and 2.0 (g/g). Water was passed into the second stage by a syringe pump once the temperature of the first stage reached 300 °C, which was the beginning of the major weight loss of waste tyre [16]. The steam flow rate was varied at 2.85, 4.74, 10.4 and 15.2 g h<sup>-1</sup>. The influence of gasification temperature was also investigated over the range of 600–900 °C in temperature increments of 100 °C. The carrier gas was  $\text{N}_2$ . The products exiting from the two stage reactor system were passed through an air-cooled condenser and two dry ice cooled condensers where the liquid products were condensed and collected. The non-condensable gases were collected with a 25 L Tedlar gas sample bag. The amounts of gaseous, liquid and char remaining after the catalytic pyrolysis-gasification of waste tyre were determined to establish the mass balance. The solid residue included the char produced from pyrolysis of the tyre collected in the first reactor, but also included any carbonaceous deposits on the walls and tubing of the second reactor in addition to coke formed on the catalyst and quartz wool catalyst support. It should be noted that the rate of gas release from the first stage pyrolysis of the tyre and interaction with steam in the second stage will not be uniform throughout the experiments since it has been shown

[18] that the volume of gas released and composition of the pyrolysis gases vary as the temperature of pyrolysis is increased. The yield and composition of gas is also influenced by the heating rate of pyrolysis. Therefore, because the injection of water and consequently steam formed were constant, the interaction of the steam with the evolved pyrolysis gases will not be uniform throughout the gasification stage.

The gases collected in the gas sample bag were analysed off-line using packed column gas chromatography (GC). Hydrocarbons from  $C_1$  to  $C_4$  were detected using a Varian 3380 gas chromatograph with a flame ionization detector (GC/FID) with 80/100 mesh Heysep packing and nitrogen carrier gas. Permanent gases were detected using two separate packed columns with a second Varian 3380 gas chromatograph with two thermal conductivity detectors (GC/TCD). Nitrogen, hydrogen, oxygen, and carbon monoxide were detected with one column with 60/80 mesh Heysep packing and argon carrier gas. Carbon dioxide was detected on a second column with 80/100 mesh column packing and argon carrier gas.

## 2.3. Characterization of materials

Temperature-programmed oxidation (TPO) of the used catalyst was conducted in a thermogravimetric analyzer (TGA) to determine the amount of carbonaceous coke deposited on the catalyst. The technique can also give information regarding the type of carbon deposited [19]. The TGA used was a Stanton-Redcroft TGA and the sample was heated at 15 °C min<sup>-1</sup> in air, and the weight changes were recorded up to a sample temperature of 800 °C with a final hold time of 10 min.

The characteristics of carbon deposited on the coked catalysts and the surface morphology of the catalyst were also examined by scanning electron microscopy (SEM). The SEM used was a Phillips XL30 Environmental.

The oil obtained from the pyrolysis-gasification of waste tyre was characterized using Fourier transform infrared spectrometry (FTIR) to determine any differences in composition in the derived oil. Functional group compositional analysis of the oils was carried out using a Thermo Scientific Nicolet S10 FTIR spectrometer. Small amounts of oil were coated onto a diamond crystal.

## 3. Results and discussion

### 3.1. Effect of catalyst: waste tyre ratio

Different catalyst:waste tyre ratios of 0.5, 1.0, 1.5 and 2.0 (g/g) were investigated for hydrogen production from the pyrolysis-catalytic gasification of waste tyres. The other operational conditions of gasification temperature and water injection rate were kept constant at 800 °C and 4.74 g h<sup>-1</sup>, respectively.

The results of the experiments in terms of product yield in relation to catalyst:waste tyre ratio are shown in Table 1. The product yields (gas, oil, or solid) were calculated in relation to the mass of waste tyres only, therefore resulting in more than 100% mass balance, where the added water will influence the gas production and therefore the mass balance. The yield of solid and oil was measured

**Table 1**  
Product yield at different catalyst:tyre ratios.

Catalyst:tyre ratio	0.5	1.0	1.5	2.0
Mass balance in relation to tyre only				
Gas/tyre (wt.%)	39.8	44.4	58.2	61.2
Solid/tyre (wt.%)	41.7	45.3	50.3	52.3
Oil/tyre (wt.%)	31.9	16.9	15.2	8.7
Mass balance (wt.%)	113.5	106.5	123.7	122.2
Reacted water (g)	0.14	0.18	0.29	0.34

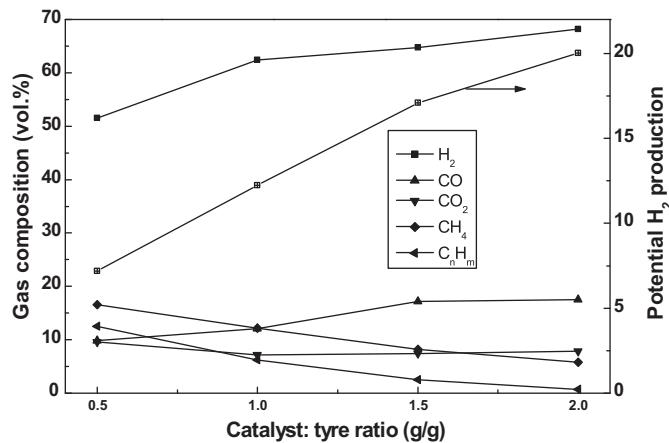
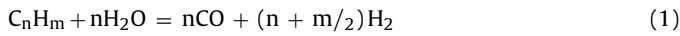


Fig. 2. Gas concentrations for different catalyst:tyre ratios.

by weighing, and the yield for gas was calculated from the appropriate gas concentration and molecular mass. In this experiment, reacted water was calculated from the concentration of CO and CO<sub>2</sub> gases; it was assumed that all the oxygen in CO and CO<sub>2</sub> gases were derived from reacted water. The data shown in Table 1 indicates that there was a significant increase in the gas yields and the amount of reacted water with increasing catalyst:waste tyre ratio. For example, the gas yield was increased from 39.8 to 61.2 wt.% and the amount of reacted water was increased from 0.14 to 0.34 g, when the catalyst:waste tyre ratio was increased from 0.5 to 2.0 (g/g). In addition, the oil yield was markedly decreased from 31.9 to 8.7 wt.% when the catalyst:waste tyre ratio was increased from 0.5 to 2.0 (g/g). The solid yield was also increased, but it should be noted that this included not only the pyrolysis char in the first reactor, but also carbon deposits in the walls and tubing of the second reactor together, quartz wool catalyst support and the coke formation on the catalyst.

The gas composition produced from the different catalyst:waste tyre ratios in the catalytic steam pyrolysis–gasification of waste tyres is shown in Fig. 2. The results indicate that the H<sub>2</sub> concentration was increased from 51.5 to 68.2 vol.%; CO concentration was increased from 9.8 to 17.6 vol.%; and there was a consequent decrease in methane concentration from 16.6 to 5.7 vol.% and hydrocarbon gases (C<sub>2</sub>–C<sub>4</sub>) significantly decreased from 11.2 to 0.7 vol.%, when the catalyst:waste tyre ratio was increased from 0.5 to 2.0 (g/g). Furthermore, the potential H<sub>2</sub> production was only 7.2 wt.% at the catalyst:waste tyre ratio of 0.5 (g/g), which increased to more than double (20.0 wt.%) at the catalyst:waste tyre ratio of 2.0 (g/g). In this work the potential hydrogen production is defined as the percentage of the hydrogen produced from the pyrolysis–gasification process in relation to the maximum theoretical amount of H<sub>2</sub> available in the tyre rubber which is estimated to be 38.7 g per 100 g tyre. It is suggested that increasing the catalyst:waste tyre ratios during the gasification process resulted in a significant increase of H<sub>2</sub> and CO content in the product gas and a sharp reduction in hydrocarbon gases, might be due to the high reaction rate of the hydrocarbon reforming (Reaction (1)).



The reacted Ni/Al<sub>2</sub>O<sub>3</sub> catalysts produced from the pyrolysis–catalytic gasification of waste tyre at different catalyst:waste tyre ratios were characterized using TGA-TPO. Fig. 3 shows the TGA-TPO and DTG-TPO results from different catalyst:waste tyre ratios. From the TGA-TPO results, the amount of coke deposited on the catalyst was 18.2, 14.6, 11.2 and 7.7 wt.% for the catalyst weight of

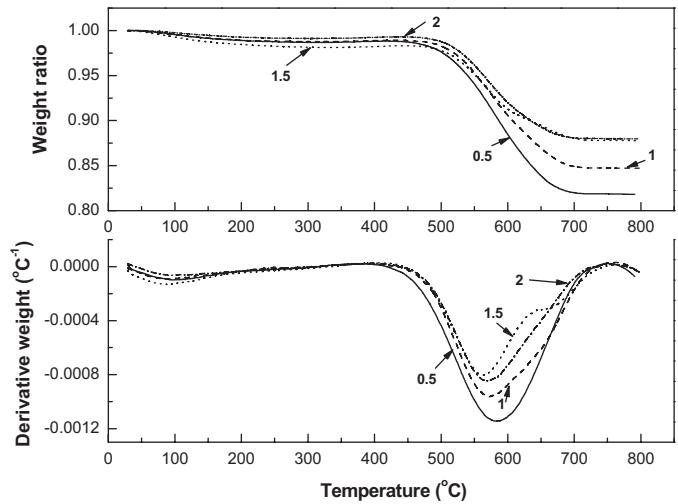


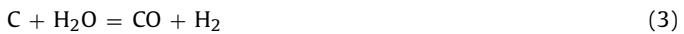
Fig. 3. TGA-TPO and DTG-TPO results of the reacted catalysts produced with different catalyst:tyre ratios.

0.5, 1.0, 1.5 and 2.0 g, respectively. The amount of coke deposited on the surface of the catalyst was calculated as follows:

$$w = \frac{(W_1 - W_2)}{W_1} \times 100 \text{ wt.\%} \quad (2)$$

where *w* is the amount of coke formed on the catalyst (wt.%); *W*<sub>1</sub> is the weight of reacted catalyst after moisture evaporation in the TGA; *W*<sub>2</sub> is the final weight of reacted catalyst after oxidation in the TGA.

It appears that the coke deposited on the surface of the catalyst reduced when the catalyst:waste tyre ratio was increased from 0.5 to 2.0 (g/g) (Fig. 3). It is suggested that increasing the amount of catalyst used in the gasification stage, more carbon was gasified by steam according to the following reactions:



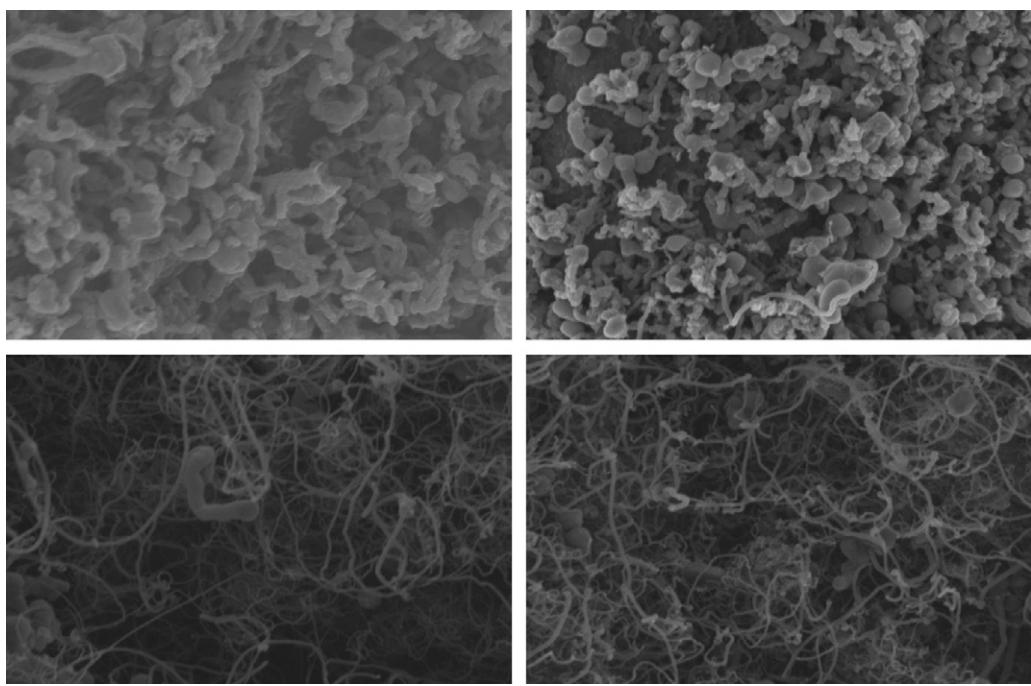
Similar results were also obtained by Wu and Williams [20] during catalytic pyrolysis–gasification of waste plastics at a gasification temperature of 800 °C and using Ni–Mg–Al as a catalyst.

The DTG-TPO results showed that a main carbon oxidation peak was observed at around 580 °C with a secondary peak developing at higher temperatures which could correspond to the burn off of filamentous carbon [19,21], which filamentous carbons were observed to be present on the catalyst by the SEM analysis of the reacted Ni/Al<sub>2</sub>O<sub>3</sub> catalyst (Fig. 4). Fig. 4 shows that as the catalyst:waste tyre ratio was increased, the formation of filamentous carbons became more pronounced with longer carbon filaments being formed as the catalyst:waste tyre ratio was increased.

### 3.2. Effect of gasification temperature

The gasification temperatures of 600, 700, 800, and 900 °C were investigated for the production of hydrogen from the pyrolysis–gasification of waste tyres, while the catalyst:waste tyre ratio and the water flow rate were maintained at 0.5 (g/g) and 4.74 g h<sup>-1</sup> respectively.

The product yield from the catalytic steam pyrolysis–gasification of waste tyres at different gasification temperatures are shown in Table 2. Again, the data are presented in terms of product yield in relation to tyre rubber only. It is shown that the gas yield in relation to the mass of waste tyres largely increased from 14.3 wt.% to 56.8 wt.% when the gasification temperature was increased from 600 to 900 °C. From Table 2, only 0.04 g of water was consumed

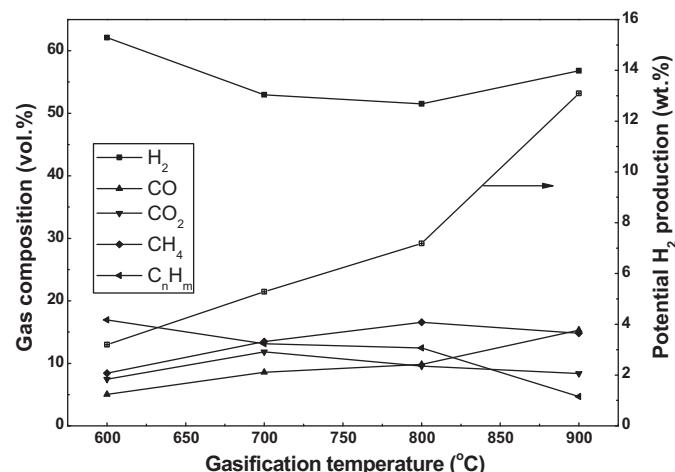


**Fig. 4.** SEM results of the reacted catalysts with different catalyst:tyre ratios.

for the gasification temperature of 600 °C. The amount of reacted water increased to 0.26 g when the gasification temperature was increased to 900 °C. However, the oil yield significantly decreased from 38.6 wt.% to 19.5 wt.% when the gasification temperature was increased from 600 to 900 °C. Patabhi Raman et al. [12] investigated the steam gasification of shredded rubber tyres using a pilot scale fluidized bed reactor. They found that by increasing the gasification temperature from 627 to 787 °C, the gas yield was increased, the liquid yield was decreased and the char yield was almost constant. The decrease of liquid yield with increasing gasification reaction temperature has also been reported by Leung and Wang [14] for the gasification of tyre powder using a laboratory-scale fluidized-bed gasifier. They reported that by increasing the temperature, the cracking of heavy hydrocarbons was increased resulting in a reduction in liquid yield.

The gas composition from the catalytic steam pyrolysis-gasification of waste tyres at different gasification temperatures is shown Fig. 5. The H<sub>2</sub> concentration decreased when the gasification temperature was increased from 600 to 800 °C, and then increased with an increase in gasification temperature to 900 °C. However, the potential H<sub>2</sub> production was increased from 3.2 to 13.1 wt.% over the same temperature range. The CO concentration increased and the hydrocarbon gases decreased, when the gasification temperature increased (Fig. 5). Portofino et al. [22] investigated the effect of reaction temperature (between 550 and 750 °C) in the catalytic steam gasification of waste tyres using a bench-scale rotary kiln reactor and commercial nickel catalyst and nickel/olivine as a

catalyst. They found that the highest H<sub>2</sub> concentration was obtained at 650 °C and the catalytic gasification process would be dominated by the reverse water gas shift reaction above this temperature. Similar results were obtained by Ming et al. [23] during the catalytic steam reforming of iso-octane, gasoline and hexadecane between 650 and 800 °C. They found that the highest H<sub>2</sub> concentration occurred at a temperature of about 650 °C and then decreased as the temperature increased. They also found that although the high hydrogen concentration was obtained at low reaction temperature, this was not desirable because of the low conversion of these hydrocarbons. It has been suggested [20] that the hydrogen concentration was mainly controlled by the reaction of decomposition of hydrocarbons at gasification temperatures lower than 700 °C and by the water gas shift reaction at temperatures higher than 700 °C during the catalytic steam pyrolysis-gasification process of plastic waste over the temperature range 600–900 °C. In the experiments reported here, it is suggested that the hydrogen concentration was mainly controlled by two reactions during the increase of



**Fig. 5.** Gas concentration for different gasification temperatures.

**Table 2**  
Product yield at different gasification temperatures.

Gasification temperature (°C)	600	700	800	900
Mass balance in relation to tyre only				
Gas/tyre (wt.%)	14.3	30.6	39.8	56.8
Solid/tyre (wt.%)	43.3	44.5	41.7	39.6
Oil/tyre (wt.%)	38.6	33.1	31.9	19.5
Mass balance (wt.%)	96.2	108.2	113.5	116.0
Reacted water (g)	0.04	0.11	0.14	0.26

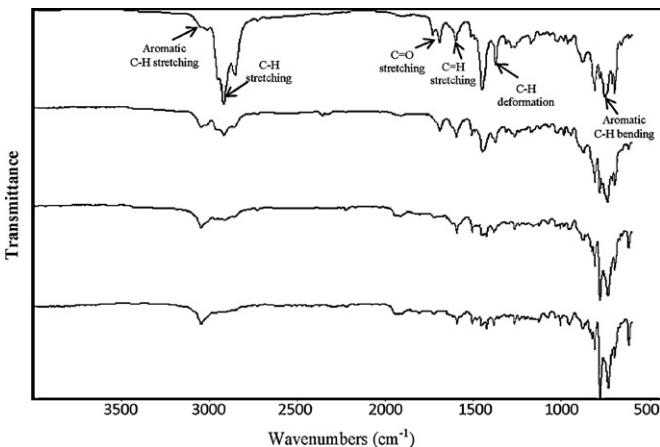


Fig. 6. FTIR spectra of the derived oil at different gasification temperatures; (a) 600 °C; (b) 700 °C; (c) 800 °C; (d) 900 °C.

gasification temperature. For the gasification temperature less than 800 °C, the reverse water gas shift reaction (Reaction (5)) might be more important than the reaction of decomposition of hydrocarbons which resulted in lower concentrations of H<sub>2</sub> and higher concentration of CO. While for the gasification temperature higher than 800 °C, the decomposition of hydrocarbons became more important for hydrogen formation, which would explain the increase in H<sub>2</sub> concentration and also the major reduction in oil yield which occurred when the gasification temperature was increased from 800 to 900 °C.



The oil produced during pyrolysis-catalytic gasification of waste tyres at the gasification temperature of 600, 700, 800 and 900 °C were analysed using FTIR spectrometry. The FTIR spectra of the oil obtained at different gasification temperatures are shown in Fig. 6. The aliphatic C–H stretching vibrations at 2800–3000 cm<sup>−1</sup> and C–H deformation vibrations at 1350–1475 cm<sup>−1</sup> indicate the presence of alkanes. The C=C stretching vibrations at 1575–1675 cm<sup>−1</sup> assigned to the presence of alkenes. The peaks at 650–900 cm<sup>−1</sup> is indicative of aromatic C–H bending and the peak at 3070 cm<sup>−1</sup> is indicative of aromatic C–H stretching. The C=O stretching vibrations at 1650–1750 cm<sup>−1</sup> can be assigned to the presence of ketones or aldehydes. From Fig. 6, it appears that there were some changes in peak intensities, and therefore compositions of the oils, as the gasification temperature was increased. For example, the peak at 2800–3000 cm<sup>−1</sup> and at 1350–1475 cm<sup>−1</sup> assigned to a C–H group such as –CH<sub>3</sub>, –CH<sub>2</sub> and –CH becomes reduced in intensity as the temperature was increased from 600 °C to 900 °C. The 650–900 cm<sup>−1</sup> and 3070 cm<sup>−1</sup> peak indicative of aromatic groups increase in intensity as the temperature was increased [24,25]. In addition, the 1650–1750 cm<sup>−1</sup> peaks indicative of ketones or aldehydes, show a decrease in intensity as the gasification temperature was raised to 900 °C.

Fig. 7 shows the TGA-TPO and DTG-TPO results in relation to different gasification temperatures. From the TGA-TPO results, the amount of coke deposited on the catalyst was 15.4, 20.8, 18.2 and 18.2 wt.% for the gasification temperature of 600, 700, 800 and 900 °C, respectively. It was found that the lowest coke formation was obtained at the gasification temperature of 600 °C. La Cava et al. [26] investigated the carbon deposition from ethane, *n*-hexane, benzene and toluene on nickel/alumina catalyst over the temperature range 450–800 °C. They observed that no deactivation by carbon deposition occurred below 625 °C which they explained as the diffusion of the carbon away from the surface once it was formed. Baker et al. [27] investigated the nucleation and the growth

of carbon on a nickel catalyst during the decomposition of acetylene. They reported that the nickel film nucleated to form small particles and a flocculent amorphous deposit was formed around these particles at low temperature (around 600 °C).

It was found that with increasing gasification temperature from 600 to 700 °C, the coke formation on the surface of the catalyst increased (Fig. 7). Wang et al. [28] also found that the deposited amounts of carbon on the surface of the catalyst increased with increasing reaction temperature from 550 to 750 °C during the catalytic steam reforming of bio-oil which were generated from the fast pyrolysis of biomass. La Cava et al. [26] reported that at temperatures between 625 and 725 °C, carbon formation was greater than that expected as long as the surface of nickel particles were coated with carbon. From the DTG-TPO experiments (Fig. 7), there appears to be a change in the type of carbon on the catalyst surface with change in gasification temperature. At 600 °C the main carbon oxidation peak corresponding to monoatomic carbon dominates and at 900 °C gasification temperature the main oxidation peak was observed at ~680 °C corresponding to filamentous carbon [19,20,29]. At 700 and 800 °C two types of carbon were formed on the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst.

When the gasification temperature was higher than 700 °C, less coke formation was observed (Fig. 7). The same result was obtained by Wu et al. [30] during catalytic steam reforming of fast pyrolysis bio-oil in a two-stage fixed bed reactor system using Ni/Mg as a catalyst. Wu and Williams [20] suggested that the coke gasification reactions could prevail with the Ni-Mg-Al catalyst at higher gasification temperature. Salehi et al. [31] also found that a decreasing trend was observed for carbon deposition with increasing temperature from 750 to 950 °C over Ru–Ni/Al<sub>2</sub>O<sub>3</sub> catalyst during the catalytic steam reforming of bio-oil. They suggested that the Boudouard and thermal decomposition reactions moved towards the reverse direction of carbon formation by increasing the temperature. In these experiments, it is suggested that the reverse Boudouard reaction (Reaction (6)) may have some importance for reducing the carbon deposited in Ni/Al<sub>2</sub>O<sub>3</sub> catalyst when the gasification temperature is higher than 700 °C, which would explain the decrease in CO<sub>2</sub> concentration.



### 3.3. Effect of water flow rate

Four water injection flow rates, 2.85, 4.74, 10.4 and 15.2 g h<sup>−1</sup>, were investigated to determine their influence on hydrogen production. The catalyst weight and gasification temperature were maintained at 0.5 (g/g) and 800 °C respectively.

The product yield of the experiments corresponding to different water flow rates is presented in Table 3. From Table 3, the gas yield and the amount of reacted water increased when the water injection rate was increased from 2.85 to 10.4 g h<sup>−1</sup>, then the gas yield and the reacted water slightly decreased with a further increase in water injection rate to 15.2 g h<sup>−1</sup>. However, the oil yield decreased from 32.8 wt.% to 29.2 wt.% with increasing water injection rate from 2.85 to 10.4 g h<sup>−1</sup>, then the oil yield slightly increased to 30.0 wt.% with a further increase in water injection to 15.2 g h<sup>−1</sup>.

The gas composition results in relation to injected water flow rate are shown in Fig. 8. From Fig. 8, there was only a small influence of water injection flow rate on gas yield and composition, for example, the H<sub>2</sub> concentration increased slightly from 50.60 to 52.12 vol.% and CO increased from 9.64 vol.% to 11.38 vol.% and methane and hydrocarbon gases (C<sub>2</sub>–C<sub>4</sub>) were decreased when the water injection rate was increased from 2.85 to 10.4 g h<sup>−1</sup>. Fig. 8 also shows that the potential H<sub>2</sub> production showed the same trend as the H<sub>2</sub> concentration, which increased as the water injection rate increased to 10.4 g h<sup>−1</sup> and reduced with higher water

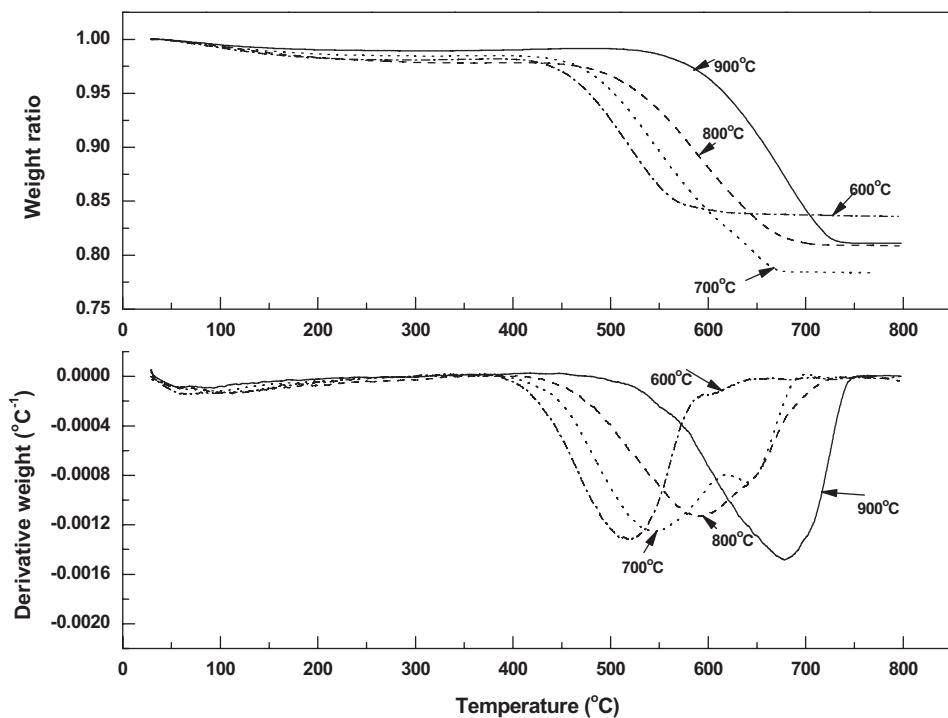


Fig. 7. TGA-TPO and DTG-TPO results of the reacted catalysts produced at different gasification temperatures.

**Table 3**  
Product yield at different water injection rates.

Water injected rate (g h⁻¹)	2.85	4.74	10.4	15.2
Mass balance in relation to tyre only				
Gas/tyre (wt.%)	30.4	39.8	48.4	47.1
Solid/tyre (wt.%)	43.5	41.7	37.5	35.1
Oil/tyre (wt.%)	32.8	31.9	29.2	30.0
Mass balance (wt.%)	106.6	113.5	115.1	112.2
Reacted water (g)	0.09	0.14	0.19	0.18

injection rate. Li et al. [32] found the same trend during the catalytic steam gasification of palm oil wastes in a fixed bed reactor using a trimetallic catalyst. They reported that with increasing steam injection, an excessive steam quantity resulted in a decreased reaction temperature which then caused gas quality degradation. Wu and Williams [33] suggested that with extra water content in the

gasification process, the cracking of large molecular weight compounds might be reduced causing a lower hydrogen production. It was suggested that the hydrocarbon reforming reaction (Reaction (1)) could prevail for a water injection rate less than 10.4 g h⁻¹, which would explain the increase in H<sub>2</sub> and CO concentrations and the reduction in methane and hydrocarbon gases (C<sub>2</sub>–C<sub>4</sub>). While the reverse water gas shift reaction (Reaction (5)) becomes more dominant than the hydrocarbon reforming reaction for the water injection rate higher than 10.4 g h⁻¹, which would explain the increase in CO<sub>2</sub> concentration and the decrease in CO concentrations. Furthermore, the methanation reaction (Reaction (7)) may also have some importance for the water injection rate greater than 10.4 g h⁻¹, which would explain the decrease in H<sub>2</sub> concentration and also the increase in methane concentration [34].



Fig. 9 shows the TGA-TPO and DTG-TPO results from different water injection rates. From the TGA-TPO results, the amount of coke deposited on the catalyst was 18.3, 18.3, 8.9 and 8.7 wt.% for the water injection rates of 2.85, 4.74, 10.4 and 15.2 g h⁻¹, respectively. It appears that the amount of coke deposited on the catalyst reduced with increasing water injection rate. It is suggested that the presence of water reduces the residence time of hydrocarbon fragments which form coke deposits [35].

The DTG-TPO results showed that two main oxidation peaks were observed which represent the different types of carbons deposited on the catalyst surface (Fig. 9). It appears that the higher oxidation peak of the filamentous type carbon was reduced at the higher of water injection rate whereas the lower oxidation peak remains almost constant. Similar results were obtained by Wu and Williams [33] where the steam injection rate in the gasification of polypropylene with a Ni/ZSM-5 catalyst was investigated. However, Demicheli et al. investigated the deactivation of a Ni/Al<sub>2</sub>O<sub>3</sub> catalyst by coke formation and reported that the filamentous carbon was not affected by steam [36].

It is suggested that the stoichiometric amount of steam could be affected by the catalyst in the gasification process [37]. While

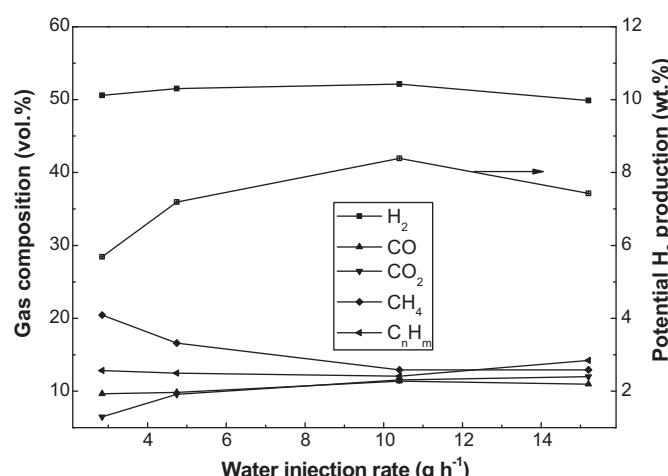


Fig. 8. Gas concentration at different water injection rates.

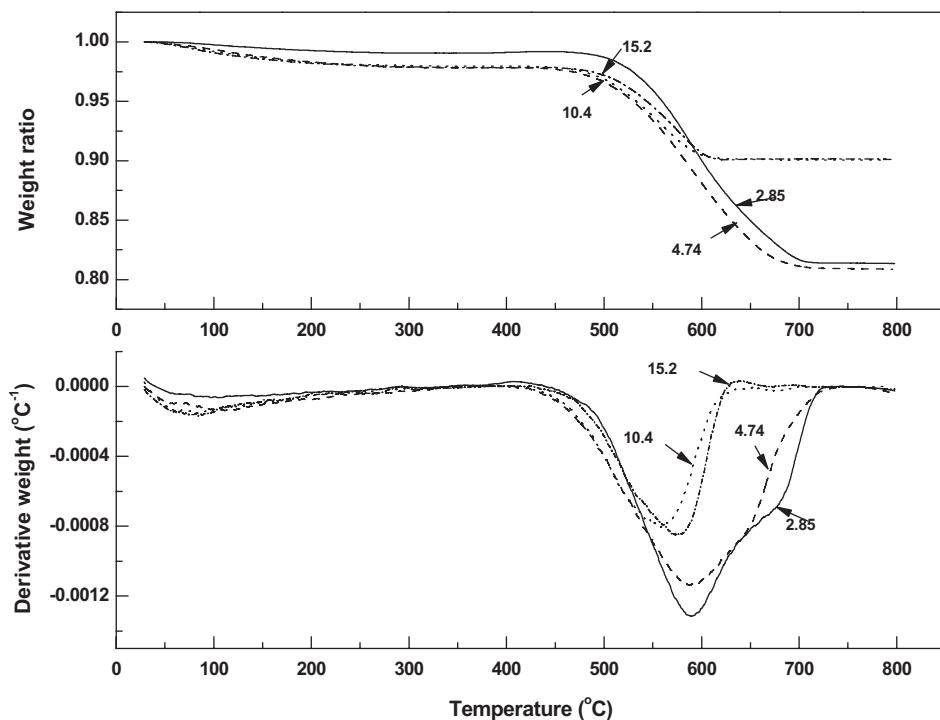


Fig. 9. TGA-TPO and DTG-TPO results of the reacted catalysts produced with different water injection rates.

the results obtained in this work suggest that the stoichiometric amount of steam should be between 4.74 and 15.2 g h<sup>-1</sup> either for the potential H<sub>2</sub> production or for the amount of coke deposited on the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst.

This paper has shown that the amount of coke deposited on a Ni/Al<sub>2</sub>O<sub>3</sub> catalyst was 18.2 wt.% and the potential H<sub>2</sub> production was 7.2 wt.% at a catalyst:waste tyre ratio of 0.5, gasification temperature of 800 °C and steam injection rate of 4.74 g h<sup>-1</sup>. However, Wu and Williams [38] found that the amount of coke deposited on the identical Ni/Al<sub>2</sub>O<sub>3</sub> catalyst was 11.2 wt.% and the potential H<sub>2</sub> production was 26.7 wt.% using polypropylene as the feed stock and under the same operation conditions. Furthermore, our previous work [16] showed 31 wt.% coke and 14.03 wt.% potential H<sub>2</sub> production for tyre using a Ni-Mg-Al as the catalyst but for polypropylene the results were 3.9 wt.% coke and 53.1 wt.% potential H<sub>2</sub> production using the same catalyst [19]. Coll et al. [39] investigated the reactivity of benzene, toluene, anthracene, pyrene and naphthalene and their tendency to coke formation during catalytic steam reforming using a commercial Ni based catalyst. They found that the order of reactivity was benzene > toluene > anthracene > pyrene > naphthalene. They found also that by increasing the number of aromatic rings in the molecule, the tendency to coke formation was increased. Rostrup-Nielsen and Tottrup [40] have reported data for a range of hydrocarbons which showed that ethylene and aromatic compounds have extremely higher tendency to produce coke compared to aliphatic components. In general, it seems that the aliphatic components are more reactive and results in less coke formation than the aromatic components which explains the high amount of coke deposited on the catalyst and the low potential H<sub>2</sub> production when processing waste tyres compared with using polypropylene during the two stage steam catalytic pyrolysis-gasification process. It should also be noted that the presence of sulphur has also been reported to affect the process by reducing the potential H<sub>2</sub> production and increasing coke formation on the catalyst [23,41–43].

#### 4. Conclusions

Hydrogen production from waste tyres has been investigated using a two-stage pyrolysis-catalytic steam gasification process using a Ni/Al<sub>2</sub>O<sub>3</sub> catalyst. The influence of the catalyst:waste tyre ratio, gasification temperature and water injection rate on hydrogen production and coke formation were investigated. The following results have been obtained:

- (1) The catalyst:waste tyre ratio showed a noticeable influence on the product yield and gas concentration for the catalytic steam pyrolysis-gasification of waste tyre. The gas yield, reacted water and the potential H<sub>2</sub> production were increased and the oil yield was largely decreased when the catalyst:waste tyre ratio increased. The coke deposited on the surface of the catalyst reduced from 18.2 to 7.7 wt.%, when the catalyst:waste tyre ratio was increased.
- (2) With increasing gasification temperature from 600 to 900 °C, the gas yield related to the mass of waste tyre was significantly increased from 14.3 wt.% to 56.8 wt.% and the potential H<sub>2</sub> production was increased from 3.2 to 13.1 wt.%. The CO concentration increased and the hydrocarbon gases decreased, when the gasification temperature was increased. The highest amount of coke deposited on the catalyst was 20.8 wt.% at a gasification temperature of 700 °C.
- (3) The increasing input of steam to the catalyst gasification bed was found to be favourable for H<sub>2</sub> concentration and the potential H<sub>2</sub> production. However, with excessive water injection rate, H<sub>2</sub> concentration and the potential H<sub>2</sub> production were reduced. The amount of coke deposited on the catalyst was reduced from 18.3 to 8.7 wt.%, when the water injection rate was increased from 2.85 to 15.2 g h<sup>-1</sup>. It is suggested that more carbon was gasified with increasing water injection rate.
- (4) There was significant formation of carbonaceous coke on the catalyst and was shown by temperature-programmed oxidation analysis and scanning electron microscopy to be

composed of two types of carbon, monoatomic carbon and filamentous carbon.

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